

PATENT SPECIFICATION

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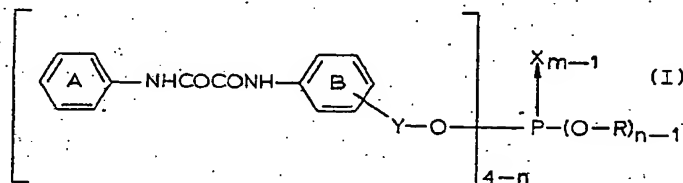
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 (72) Inventors KURT HOFER and DR. RUDOLF MOESCH



(54) N,N'-DIARYLOXAMIDES CONTAINING PHOSPHORUS AND A PROCESS FOR PRODUCING THEM

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle/Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new organic phosphorus compounds, and processes for producing them. The present invention provides organic phosphorus compounds of formula



where each benzene nucleus A and/or each benzene nucleus B, independently, may be substituted,

m is 1 or 2,

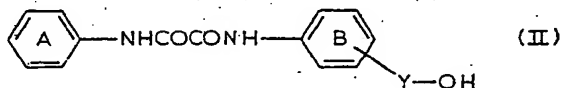
n is 1, 2 or 3,

each R, independently, is a hydrogen atom or an unsubstituted or substituted alkyl, cycloalkyl or phenyl radical,

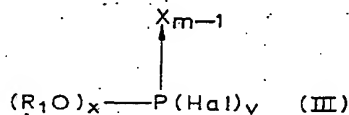
X is O or S, and

each Y, independently, is a direct single bond or an alkylene radical which is bound to the benzene nucleus B either directly or through an oxygen or sulphur atom and which may be interrupted by one or more oxygen atoms.

A compound of formula (I) can be produced by (a) condensing a compound, or different compounds, of formula



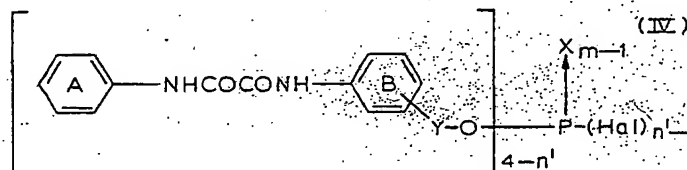
wherein benzene nucleus A and/or benzene nucleus B, independently, may be substituted, and Y is as defined above, with a compound of formula (III)



[Price 25p]

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where X and m are as defined above, Hal is a halogen atom, each R₁, independently, is an unsubstituted or substituted alkyl, cycloalkyl or phenyl radical, and x and y are each 0, 1, 2 or 3, the sum of x and y being 3, in a molar ratio of y:1 when y is other than 0, or in a molar ratio of from 1:1 to x:1 when y is 0, to produce a compound of formula (I), with the proviso that when n is 2 or 3, then R is other than hydrogen, or (b) condensing a compound of formula (IV).



wherein each benzene nucleus A and/or each benzene nucleus B, independently, may be substituted,

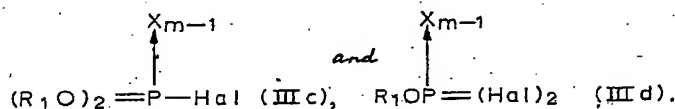
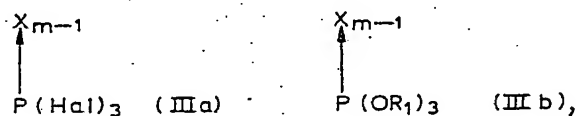
X, Y and m are as defined above, Hal is a halogen atom, and n' is 2 or 3, with a compound, or compounds, of formula (V)

HOR

(V)

wherein R is as defined above, in a molar ratio of 1:n'—1.

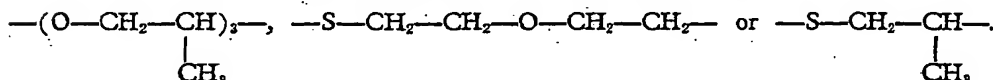
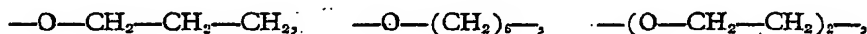
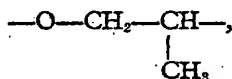
Examples of compounds of formula (III) are



wherein R₁, X and m are as defined above.

The benzene nuclei A and B in formulae (I) and (II) may be unsubstituted or substituted.

Suitable substituents include straight or branched alkyl and alkoxy radicals, cycloalkyl radicals and halogen atoms. In the preferred compounds of formula (I) the benzene nucleus A is substituted by one or two alkyl radicals, neither of the said alkyl radicals containing more than 9 carbon atoms, by one or two alkoxy radicals, neither of the said alkoxy radicals containing more than 16 carbon atoms and/or by one hydroxyl group, which is in ortho-position with respect to the N atom or to a tertiary alkyl radical. The benzene nucleus B is preferably unsubstituted or substituted by a methyl group, m is preferably 1 and n 1 or 2. Y is preferably the direct single bond, though it may represent ethylene, 1,2-propylene, 1,3-propylene, 1,4-butylene, —O—CH₂—CH₂—,



Examples of unsubstituted or substituted alkyl radicals R and substituents on the benzene nuclei A and B are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-amyl, sec-amyl, iso-amyl, tert-amyl, n-hexyl, n-heptyl, n-octyl, 2-octyl, 2-ethylhexyl, tert-octyl, tert-nonyl, n-decyl, n-dodecyl, tert-dodecyl, n-tetradecyl, cetyl, stearyl, behenyl, trifluoromethyl, 2,2-difluoroethyl, 2-cyanethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-n-butoxyethyl, 3-methoxypropyl, 2-(2'-ethoxyethoxy)-ethyl, 2-(2'-n-butoxyethoxy)-ethyl, 2-methylmercaptoethyl, 3-methylmercaptoethyl and tetrahydrofurfuryl. Alkyl radicals which, together with any substituents present, contain not more than 8 carbon atoms are preferred.

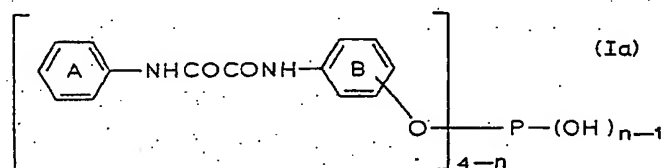
Suitable cycloalkyl radicals R or substituents on the benzene nuclei A and B of formula (I) are, for example, cyclopentyl, cycloheptyl and in particular unsubstituted or substituted cyclohexyl radicals such as cyclohexyl itself, 4-methylcyclohexyl, 2,5-, 2,6-, 3,4- and 3,5-dimethylcyclohexyl.

The preferred meaning of R is hydrogen.

Like the alkyl radicals in the general formula (I), the alkoxy radicals in the benzene nuclei A and B, jointly with any substituents present, may have 1 to 22 or preferably 1 to 8 carbon atoms. The following may be named as examples: methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, tert-butoxy, sec-butoxy, n-amyl-oxy, iso-amyl-oxy, tert-amyl-oxy, n-hexyloxy, n-octyloxy, 2-octyloxy, 2-ethylhexyloxy, n-decyloxy, n-dodecyloxy, tert-dodecyloxy, cetyloxy, stearyloxy, behenyloxy, methoxy-ethoxy, 2-n-butoxyethoxy, 2-cyanethoxy, 2-(2'-ethoxyethoxy)-ethoxy and 2-(2'-n-butoxyethoxy)-ethoxy.

When one or both of the benzene nuclei A and B is or are substituted by a halogen atom, the halogen atom may for example, be bromine or preferably chlorine.

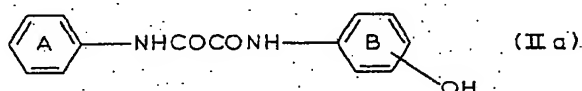
A preferred range of compounds within formula (I) are those of formula



wherein n is 1 or 2,

each benzene nucleus A, independently, is unsubstituted or substituted by one or two alkyl radicals containing not more than 9 carbon atoms, by one or two alkoxy radicals containing not more than 16 carbon atoms and/or by one hydroxyl group which is in the ortho position with respect to the N atom or to a tertiary alkyl radical, and each benzene nucleus B, independently, is unsubstituted or substituted by a methyl group.

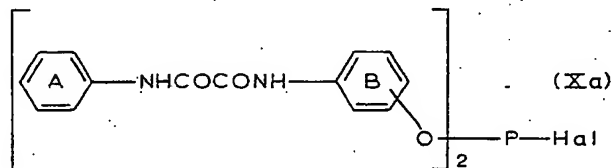
Such compounds wherein n is 1 can be prepared by condensing a compound, or different compounds, of formula (IIa)



wherein the benzene nuclei A and B are as defined above,

with phosphorus trichloride or phosphorus tribromide in the molar ratio 3:1.

Such compounds wherein n is 2 can be prepared by reacting a compound of formula (Xa)



wherein the benzene nuclei A and B are as defined above,

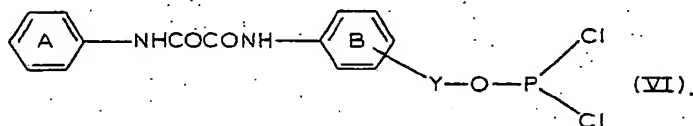
and Hal is a halogen atom,
with water in equimolar proportions.

Especially valuable compounds of formula (I) are those in which both m and n stand for 1 and those in which m stands for 1 and n for 2.

The starting compounds of formulae (II), (IIa), (III) and (V) are known or can be produced in a manner analogous with known methods.

The process of production described above involves the synthesis of esters of phosphorous, phosphoric or thiophosphoric acid. These syntheses proceed by analogy with known methods, which are collectively described in the literature, cf. K. Sasse, "Organische Derivative phosphorhaltiger Mineralsäuren" in "Handbuch der Methoden der organischen Chemie" (Houben-Weyl), 4th Edition, Vol. XII/2, Part 2, pp. 5-82, 143-208, 226-274, 299-374, 587, 598-602 and 623-651.

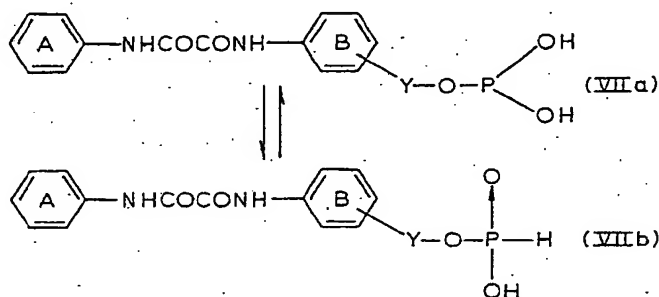
Phosphorous acid esters of formula (I) in which m stands for 1 and n for 3 can be obtained by reacting a compound of formula (II) with excess phosphorus trichloride to produce, as an intermediate, a corresponding phosphorous acid ester dichloride of formula



For this reaction it is convenient to enter the phosphorus trichloride into the vessel first and then to add gradually the hydroxyl compound of formula (II), using the phosphorous trichloride in at least four times the molar amount. The reaction is carried out in the absence of moisture. The optimum starting temperature is 20-30°C and towards the end of the reaction the temperature is raised, optionally to the boiling point of the phosphorus trichloride, until the hydroxyl compound disappears and the reaction is complete. If a compound of formula (II) containing the phenolic hydroxyl group is employed, the reaction proceeds at a relatively slow rate, so in such cases catalysts such as magnesium chloride can be used. If a compound of formula (II) containing an alcoholic hydroxyl group is employed it is advisable to remove from reaction the hydrogen chloride formed as by-product, either by introducing an inert gas or by adding a hydrogen halide acceptor, such as a tertiary amine or pyridine. Further, to prevent side-reactions it is advisable to commence the reaction at low temperature, for example at 0 to -15°C. These reactions run analogously when phosphorus tribromide is used in place of phosphorus trichloride, the resulting compounds of formula (VI) having two bromine atoms instead of chlorine atoms.

The halogen atoms in the compounds of formula (VI) can be replaced by hydroxyl groups, in which case the final products are phosphorous acid monoesters. It is advisable to carry out this hydrolysis with a theoretical amount of water and to neutralize the hydrochloric acid formed, either during or immediately after the reaction, with an acid-binding agent such as pyridine. By taking this precaution decomposition of the phosphorous acid monoesters can be avoided.

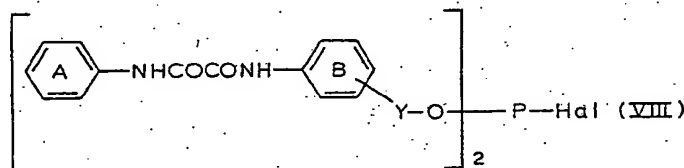
The latter have one of the following structural formulae:



Alternatively, the intermediates of formula (VI) can be reacted with unsubstituted or substituted phenols to yield compounds of formula (I) in which m stands for 1, n for 3 and each R independently for unsubstituted or substituted phenyl. This reaction

can be carried out with a theoretical amount or with an excess of the selected phenol. The reaction temperature is preferably high, e.g. 100—180°C, depending on the acidity of the starting phenol. Phenols of higher acidity necessitate heating to more elevated temperatures to reach the end-point of the reaction. In this mode of operation a hydrogen halide is split off and escapes from the reaction mixture. In order to avoid hydrolytic side-reactions it is important to exclude moisture in this reaction. Acid-binding agents can be used to bind the hydrogen halide liberated. This particular mode of operation of the process is also preferred for reacting compounds of formula (VI) with alcohols instead of phenols, which process results in compounds of formula (I) in which m stands for 1, n for 3 and each R independently for unsubstituted or substituted alkyl radicals. Asymmetrical phosphorous acid triesters of this type in which each R of formula (I) independently represents an alkyl radical having at least 6 carbon atoms, and more than one value of R is present, are highly effective stabilizers for polyalkylenes as they are very soluble in these polymers and do not migrate.

Using a process analogous with the above procedure yielding the phosphorous acid ester dihalides of formula (VI), phosphorus diester halides of formula



can be obtained. In these intermediates again the halogen atoms may be replaced by unsubstituted or substituted phenoxy or alkoxy radicals, as stated above in reference to compounds of formula (VI). In this way final products of formula (I) are formed in which m is 1 and n is 2.

If the halogen atom in the phosphorous acid diester halides of formula (VIII) is replaced by the hydroxyl group, the corresponding phosphorous acid diesters are obtained. This transformation takes place fairly easily at room temperature or with cooling to lower temperatures, using a theoretical amount of water and optionally an acid-binding agent such as a trialkylamine. The same esters are formed when compounds of formula (VIII) are reacted with alcohols instead of water in the absence of an acid-binding agent, the alcohols being converted into the corresponding alkyl halides.

Compounds of formula (I) in which m and n are both 1 are obtained when 3 mols of a compound of formula (II) are reacted with 1 mol of a phosphorus halide, preferably phosphorous trichloride. If compounds of formula (II) containing phenolic hydroxyl groups are employed for this reaction it does not proceed at any great speed and generally it is necessary to raise the temperature to about 100° to 200°C in order to reach the end-point. Under these conditions the hydrogen halide splits off in the reaction and escapes from the mixture. In order to promote its escape the reaction can be carried out in the presence of an inert solvent such as an aromatic hydrocarbon of high boiling point so that the mixture remains in the form of a liquid of low viscosity to the end of the reaction. If starting compounds of formula (II) containing alcoholic hydroxyl groups are chosen, an acid-binding agent such as a trialkylamine is necessary to bind the hydrohalic acid formed as by-product.

Starting from phosphorus trihalides and a mixture of different hydroxyoxamides of formula (II) and using an analogous process, asymmetrical phosphorous acid esters or mixtures of esters of phosphorous acid can be produced which conform to formula (I) and in which both m and n are 1. Similarly, asymmetrical esters of phosphorous acid are formed when a phosphorus trihalide is reacted with a mixture of hydroxyl compounds of formulae (II) and (V).

In the modes of operation of the process so far described the phosphorus halides serve as starting materials. It is however possible to start from esters of phosphorous acid of formula (IIIb), in which m is 1. Transesterification of these with compounds of formula (II) yields new esters of phosphorous acid within the present invention. It is of advantage to use a catalyst to accelerate the transesterification reaction, for example sodium phenolate, lead suboxide, calcium acetate, antimony trioxide or aluminium chloride. In order to shift the reaction equilibrium as far as possible to the right, the hydroxyl compound which is split off from the starting ester during the reaction can be continuously removed, for example by distillation in high vacuum.

The aforesaid esters of phosphorous acid which still contain oxamide groups can also be used as starting materials for the production of phosphoric acid esters containing oxamide groups. This transformation of compounds with trivalent phosphorus into others with quinquivalent phosphorus can be carried out with any of many diverse oxidizing agents. For example, the starting compounds can be oxidized with sodium hypochlorite or hydrogen peroxide in almost neutral suspension. Generally the temperature for such reactions should be only moderate, preferably below 50—60°C, to prevent side-reactions due to hydrolysis. It is often necessary to work in a water-free medium to exclude side-reactions completely. For example, oxygen can be used for oxidation, which means that the temperature has to be increased to at least 70°C for sufficiently rapid reaction. But if the medium is irradiated with actinic light at the same time sufficiently rapid oxidation can be achieved at room temperature or 30—40°C. Given the absence of moisture, sulphuryl chloride can be used for oxidation.

The phosphorous acid triesters described above are also suitable as intermediates for the synthesis of the corresponding thiophosphoric acid-O,O,O-triesters. This addition of sulphur takes place very easily with phosphorous acid triesters derived from alcohols. The reaction is exothermic and must be carried out with cooling to preclude side-reactions, notably rearrangement to O,O,S isomers. It is conducted preferably in a solvent such as benzene, ethanol or chloroform in the absence of water. If the sulphur is to be added on phosphorous acid triesters derived from phenols, higher temperatures ranging from 100° to 200°C are necessary. In these cases the solvent can normally be omitted, the reaction then being carried out in the melt. Under these conditions, isomerization to O,O,S triesters does not occur.

These thiophosphoric acid esters can also be produced by reacting thiophosphoric acid chlorides with compounds of formula (II), if desired in mixture with compounds of formula (V). As the rate of reaction is relatively slow, the hydroxyl compounds can be employed in the form of their alkali metal salts, or alternatively catalysts such as phosphorous trichloride, pyridine or copper powder can be used.

The analogous reaction in which phosphorus oxychloride is used in place of thiophosphoric acid chloride proceeds very much easier and leads to the corresponding phosphoric acid esters, which as stated above are also obtainable from the corresponding esters of phosphorous acid by oxidation.

The present invention relates further to a method of improving the stability of organic materials, especially plastics materials. Thus, the invention provides a method of improving the stability of an organic material against the action of ultraviolet light, visible light, heat or air, which comprises admixing with the organic material from 0.01 to 5% by weight of at least one compound of formula (I), as defined above, and provides an organic material which contains at least one compound of formula (I) or (Ia) as stabilizer, or contains such a stabilizer, and at least one further stabilizer or costabilizer against the action of ultraviolet light, visible light, heat or air. Of the various materials suitable for stabilization with the compounds of formula (I) or (Ia), the following may be named: cellulose acetate, cellulose acetobutyrate, polyethylene, polypropylene, polyvinyl chloride, vinyl chloride/acetate copolymer, polyamides, polystyrene, ethyl cellulose, cellulose nitrate, polyvinyl alcohol, silicon rubber, cellulose propionate, melamineformaldehyde resins, ureaformaldehyde resins, allyl casting resins, polymethyl methacrylate, polyesters and polyacrylonitrile. Also, natural products such as rubber, cellulose, wool and silk can be stabilized with these compounds.

The abovementioned organic materials may be present in the form of a film or sheet, rod, tape, panels, coatings, fibres, granules, powders or other forms, or as solutions, emulsions or dispersions. The compounds to be used as stabilizers are incorporated in or coated on the organic materials by one of the known methods. One important method of application consists in the intimate blending of the stabilizing compound with the material, for example polypropylene granules, in a kneading mill or other suitable machine and subsequent extrusion. In this way very homogeneous mixing is obtained which is important for effective protection. The mixture can be extruded in various forms, for example as film, tubing or filaments. The latter can be processed as woven textile fabrics. In this method of application the stabilizer is blended with the polypropylene before it is converted into textiles. The new stabilizers can also be applied to textile yarns and fabrics, for example from an extremely fine dispersion in water. This method of application is suitable for textiles of polyethylene terephthalate and cellulose acetate fibres.

The new stabilizers need not necessarily be added to the final polymer; they can be blended with the monomers or prepolymers prior to the synthesis giving the final polymer.

Besides their uses in, for example, clear films and plastics, the compounds of

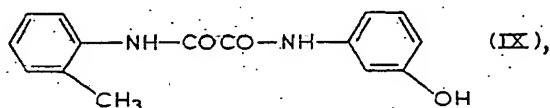
formula (I) or (Ia) are applicable in opaque, semi-opaque and translucent materials having a surface which is subject to degradation by ultra-violet radiation, atmospheric oxygen or heat. These materials include foamed plastics, opaque films and coatings, opaque papers, opaque and translucent pigmented plastics, fluorescent pigments, automobile and furniture polishes, creams, lotions and similar products, which are either clear, translucent or opaque.

The compounds of formula (I) can be employed in combination with other ultra-violet absorbers and stabilizers. Such mixtures of active substances often have a synergistic effect and safeguard the material against degradation by ultra-violet rays, visible light, heat or atmospheric oxygen over a long period of time.

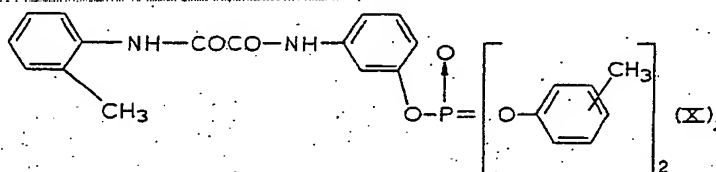
It is not always necessary to incorporate the compounds in or apply them to the material for protection. Some classes of product, for instance light-sensitive foods such as fruit, cooking oil and butter, can be protected by packaging in plastic film containing a compound of the formula (I) or (Ia).

Normally the compounds of formula (I) stabilize the material against the destructive action of ultra-violet rays, visible light, air or heat. This wide range of effectiveness makes them particularly valuable. In this respect they are found to be superior to the N,N' -diphenyloxamides known to date, which provide protection against ultra-violet radiation but are far less effective in preventing oxidative degradation by air or attack by heat.

It is not essential to produce the compounds of formula (I) in the pure form for them to be satisfactory stabilizers. The 2-methyl-3'-hydroxy- N,N' -diphenyloxamide of formula

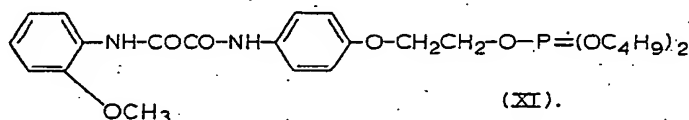


for instance, can be mixed with tricresyl phosphate in a molar ratio of 1:4 and the latter compound transesterified with heating, optionally in the presence of a catalyst such as lithium hydride or lead (II) oxide, and with continuous removal of the liberated cresol by vacuum distillation. A mixture of esters, predominantly the ester of formula



is obtained in tricresyl phosphate solution in excellent yield. The solution can be incorporated in polymers such as polyvinyl chloride or polyalkylenes, either as obtained or after dilution with further tricresyl phosphate. It acts both as stabilizer and plasticizer in these polymers. This mode of production yielding a solution of compounds of the formula (X) is highly economical, as the reaction is almost quantitative and involves no loss through isolation and purification. Moreover, a stabilizer solution of this nature can be homogeneously dispersed in the polymer with ease.

An analogous procedure can be employed to produce the new esters of phosphorous acid. For instance, 2-methoxy-4'-(hydroxyethoxy)- N,N' -diphenyloxamide and tributyl phosphite in excess can be reacted with heating and continuous removal by vacuum distillation of the butanol split off in the reaction; the product is a solution in tributyl phosphite of a phosphorous acid ester of formula



The phosphorus ester grouping in the compounds of formulae (X) and (XI) not only imparts stabilizing properties to the action of air and heat, but also increases the

solubility and the migration resistance in hydrophobic polymers such as polyvinyl chloride and polyalkylenes.

As shown in the few examples cited above, compounds of the formula (I) or (Ia) can be incorporated in organic materials by standard methods at any stage of processing, and the amounts used may vary within the wide limits of from 0.01 to 5%, or preferably 0.05 to 1%, relative to the weight of the material.

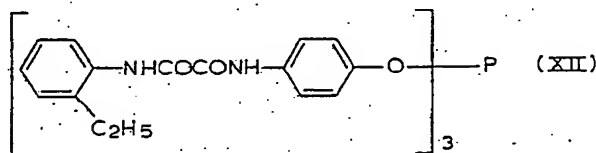
In the following Examples and Examples of Application the parts are by weight and the temperatures in degrees centigrade; m.p. denotes the melting point, λ max. the wavelength of maximum light absorption in nanometer units.

Examples of the Process of Production

Example 1.

In a vessel fitted with a reflux condenser, thermometer and stirrer 85.4 parts of 2-ethyl-4'-hydroxy-N,N'-diphenyloxamide, m.p. 211—212°, 450 parts of chlorobenzene and 23.7 parts of pyridine are mixed and raised to the boiling point in the absence of moisture. (In place of chlorobenzene, xylene or anisol can be used as solvent). At boiling temperature the greater part of the oxamide goes into solution. After cooling to 70—80° 13.8 parts of phosphorus trichloride are slowly added, on which the temperature is again raised to the boiling point. A white precipitate gradually settles out, which grows denser as the reaction continues. After 30 minutes at the boil the end-point of the reaction is reached and the mixture is allowed to cool to room temperature. The white slurry is filtered with suction, entered into a vessel equipped with a stirrer and containing about 500 parts of water at 30—40° and thoroughly stirred, filtered again with suction, washed with cold water till the water is of neutral reaction, and dried in a vacuum.

A colourless, crystalline triphosphite is obtained which has the formula



Melting point: 226—229°

Elemental analysis:	calc:	C: 65.4,	H: 5.1,	N: 9.5,	P: 3.5%
	found:	C: 65.0,	H: 5.2,	N: 9.4,	P: 3.4%

Thin layer chromatogram

Adsorption layer:	silica gel
Eluent:	chloroform/tetrahydrofuran 9:1
Flow time:	30 minutes
Development:	chlorine/o-toluidine solution
Main product:	hRf 71

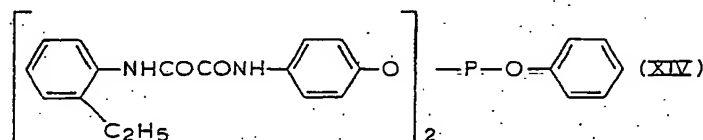
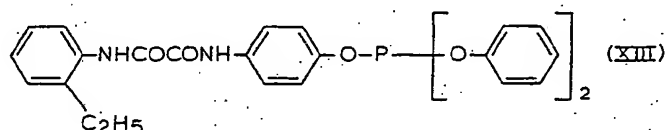
In addition minor impurities are present.

The above product can also be obtained by reacting 2-ethyl-4'-hydroxy-N,N'-diphenyloxamide with phosphorus trichloride in boiling chlorobenzene without the addition of a base, the hydrochloric acid formed being removed from the mixture by means of a current of nitrogen gas. The reaction time is longer in this case and the proportion of by-products higher.

Example 2.

In the absence of moisture a mixture of 28.4 parts of 2-ethyl-4'-hydroxy-N,N'-diphenyloxamide, m.p. 211—212°, 31 parts of triphenyl phosphite and 0.5 parts of sodium methylate is set with 80—100 parts of diphenyl ether. The batch is reacted for 2 1/2—3 hours at 150—160° with stirring in a vacuum, the vacuum being adjusted so that some diphenyl ether is continuously distilled throughout, along with the phenol split off in the reaction.

The reaction mixture is triturated with ethanol and a little water, after which it is filtered with suction, triturated with ethanol, filtered and dried. The yellowish crystalline product consists of a mixture of the compounds (XIII) and (XIV) in the quantitative ratio 3:2.

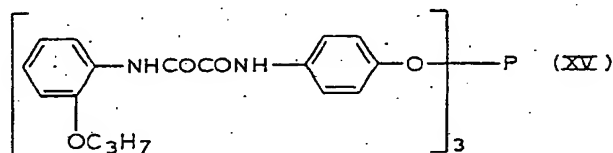


Elemental analysis

Calc.:	C: 65.4	H: 5.6	N: 7.0	P: 5.8%
Found:	C: 65.7	H: 5.1	N: 6.7	P: 5.6%

Example 3.

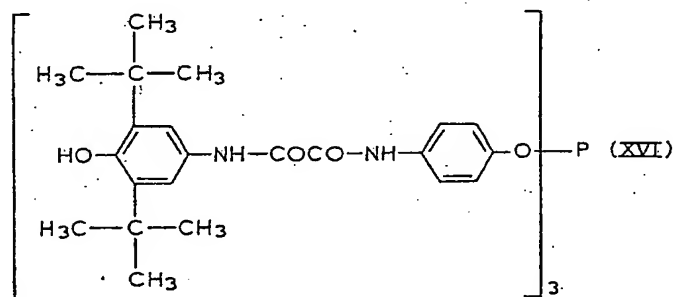
The procedure of Example 1 is employed with 94.2 parts of 2-propoxy-4'-hydroxy-N,N'-diphenyloxamide, m.p. 173—176°, and 13.7 parts of phosphorous trichloride in 400 parts of chlorobenzene and 23.7 parts of pyridine. The pyridine hydrochloride formed settles out from the boiling solution to be deposited on the wall of the reaction vessel. When the end-point of the reaction is reached the batch is allowed to cool to room temperature, on which a pale beige precipitate settles out. It is filtered with suction, thoroughly washed with water at 40—50° till neutral, filtered again with suction and dried at 80° in a vacuum. Finally it is recrystallized from dioxan solution by the addition of water to the commencement of turbidity. The colourless crystalline tri-(2'-propoxy-N,N'-diphenyloxamidyl-4)-phosphite of formula



is obtained, which melts at 189—195°.

Example 4.

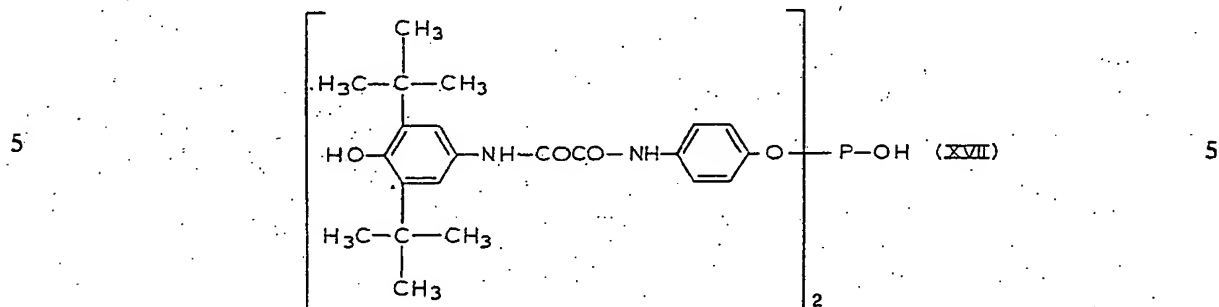
In the absence of moisture 115.2 parts of 4,4'-dihydroxy-3,5-di-(tert. butyl)-N,N'-diphenyloxamide, m.p. 198—202°, 250 parts of chlorobenzene and 23.7 parts of pyridine are mixed for 10 minutes at 120—130°. The mixture is cooled to 70—75° and 13.7 parts of phosphorus trichloride are slowly added. The batch is held at the boiling temperature for 12 hours to allow for complete reaction. It is then cooled to room temperature and the precipitated reaction product is filtered, washed with water, mixed thoroughly with ethanol, filtered and dried. The colourless crystalline compound of formula



thus obtained melts at 216—219°. In place of pyridine an equivalent amount of N,N-dimethyl cyclohexylamine can be used.

Example 5.

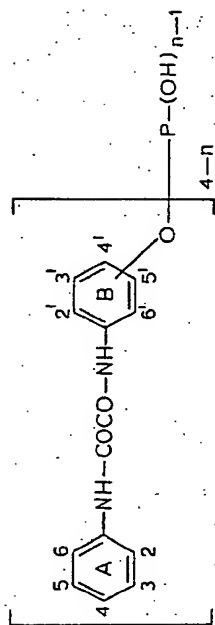
The reaction described in Example 4 is terminated at an earlier point, if desired after 1 hour, and the product worked up as in that Example. This procedure results in the diphosphite of formula



which melts at 165—175°.

The same compound is obtained when the quantitative ratio is changed and only 1.5 to 2.0 mols of the aforementioned dihydroxyoxamide are reacted with 1 mol of phosphorus trichloride.

The organic phosphorus compounds produced from phosphorus trichloride as described in Examples 1, 3, 4 and 5 are listed in the following table, where they are specified by the chemical constitution and the absorption maxima in nanometer (nm) units. The latter values are directly relevant to their ability, in practice, to absorb ultra-violet rays. The table contains additional examples of compounds which can be produced from phosphorus trichloride by processes analogous with the procedures previously described.



Exple No.	Substituent in the ring A	Substituent in the ring B	Value of n	Absorption maximum λ_{max} in nm
1	2-ethyl	4'-O-P	1	278
3	2-propoxy	4'-O-P	1	200, 300
4	3,5-di-tert.butyl-4-hydroxy	4'-O-P	1	288
5	do.	4'-O-O-BH	2	285-291, 330
6	-	4'-O-P	1	275-280
7	-	3'-O-P	1	280-285
8	2-ethoxy	2'-methoxy 4'-O-P	1	300-310
9	do...	2'-O-P-OH	2	305
10	2-octyloxy	2'-O-P	1	308
11	2-Hexadecyloxy	2'-O-P-OH	2	302-308
12	2,5-Diethoxy	3'-O-P	1	310-318
13	2-Ethyl	do	1	275-280
14	2-Hydroxy	do	1	300-310

Exple No.	Substituent in the ring A	Substituent in the ring B	Value of n	Absorption maximum λ max in nm
15	2-Ethoxy	do	1	300
16	2-Propoxy	do	1	300
17	2-Butoxy	do	1	300
18	2-Octyloxy	do	1	300
19	2-Dodecyloxy	do	1	300
20	2-Hexadecyloxy	do	1	300
21	2,4-Dimethyl	do	1	275-300
22	2,5-Dimethyl	do	1	275-300
23	2-Hydroxy	4'-O-P	1	300-310
24	2-Ethoxy	do	1	300
25	2-Butoxy	4'-O-P	1	280-300
26	2-Octyloxy	do	1	280-300
27	2-Dodecyloxy	do	1	280-300
28	2-Hexadecyloxy	do	1	300
29	2,4-Dimethyl	do	1	280
30	2,5-Dimethyl	do	1	280
31	2,5-Diethoxy	do	1	300-320

Examples of Application

Example a.

The compound of formula (XII) described in Example 1 is incorporated in unstabilized polypropylene in an amount of 0.2% and the material extrusion moulded as panels. After exposure for 300 hours in the Klimatest apparatus at 40° and 75% relative humidity the panels containing the compound (XII) are unchanged, whereas a panel without the additive shows hair cracks and brittleness.

In addition the compound (XII) within this invention imparts much greater heat stability: test mouldings of the above material containing the 0.2% of compound (XII) turn brittle after 11 days exposure at 140°, while only one day at this temperature is sufficient to cause brittleness in mouldings without the incorporated compound.

In the ageing test at 190° brittleness appears after 30 minutes in a test moulding without the additive, but not until 272 minutes in one containing the additive.

Example b.

0.5% of the phosphite described in Example 14 is incorporated in stabilized polypropylene. A moulding of this material has to be heated at 190° for 800 minutes in the oxygen ageing test before degradation of the polypropylene sets in. If in place of the phosphite of Example 14 the starting compound of that example, 2,3'-dihydroxy-N,N'-diphenyloxamide, which contains no phosphorus, is incorporated in the polypropylene, the moulded article is degraded after an exposure period of only 490 minutes.

Example c.

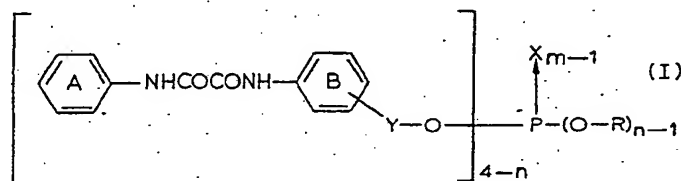
In a similar manner as in Example b the phosphite described in Example 24 is compared with the starting compound, 2-ethoxy-4'-hydroxy-N,N'-diphenyloxamide. The exposure periods necessary for degradation are 990, and 540 minutes respectively.

Example d.

The comparison made as in the Examples b and c of the stabilizing effect of the phosphite described in Example 29 with the starting material, 2,4-dimethyl-4'-hydroxy-N,N'-diphenyloxamide gives the following result: exposure periods necessary for degradation are 1240, and 362 minutes respectively.

WHAT WE CLAIM IS:—

1. Organic phosphorus compounds of formula (I)



wherein each benzene nucleus A and/or each benzene nucleus B, independently, may be substituted,

m is 1 or 2,

n is 1, 2 or 3,

each R, independently, is a hydrogen atom or an unsubstituted or substituted alkyl, cycloalkyl or phenyl radical,

X is O or S, and

each Y, independently, is a direct single bond or an alkylene radical which is bound to the benzene nucleus B either directly or through an oxygen or sulphur atom and which may be interrupted by one or more oxygen atoms.

2. Organic phosphorus compounds according to Claim 1, in which the benzene nucleus A is unsubstituted or substituted by one or two alkyl radicals, neither of the said alkyl radicals containing more than 9 carbon atoms, by one or two alkoxy radicals, neither of the said alkyl radicals containing more than 16 carbon atoms and/or by one hydroxyl group which is in the ortho position with respect to the N atom or to a tertiary alkyl radical.

3. Organic phosphorus compounds according to Claim 1 or Claim 2, in which the benzene nucleus B is unsubstituted or substituted by a methyl group.

4. Organic phosphorus compounds according to any preceding claim, in which Y is a direct single bond.

5. Organic phosphorus compounds according to any preceding claim, in which m is 1.

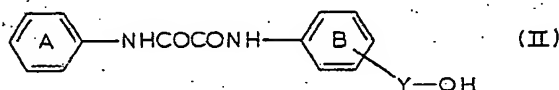
6. Organic phosphorus compounds according to any preceding claim, in which n is 1 or 2.

7. Organic phosphorus compounds according to any preceding claim, in which each R stands for a hydrogen atom.

8. A process for the production of an organic phosphorus compound of formula (I) as defined in Claim 1, which comprises

a) condensing a compound, or different compounds, of formula (II),

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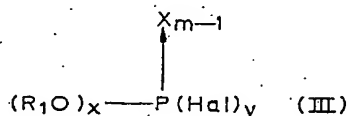


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wherein benzene nucleus A and/or benzene nucleus B, independently, may be substituted,

and Y is as defined in Claim 1, with a compound of formula (III)

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wherein X and m are as defined in Claim 1,

Hal is a halogen atom,

each R_1 , independently, is an unsubstituted or substituted alkyl, cycloalkyl or phenyl radical,

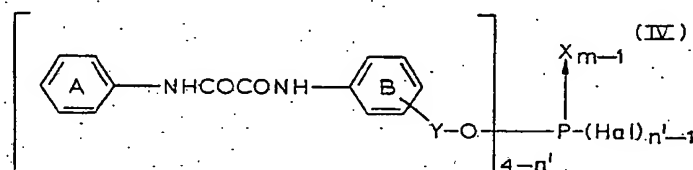
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and x and y are each 0, 1, 2 or 3, the sum of x and y being 3, in a molar ratio of y:1 when y is other than 0, or in a molar ratio of from 1:1 to x:1 when y is 0, to produce a compound of formula (I), with the proviso that when n is 2 or 3, then R is other than hydrogen,

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or b) condensing a compound of formula (IV)

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wherein each benzene nucleus A and/or each benzene nucleus B, independently, may be substituted,

X, Y and m are as defined in Claim 1,

Hal is a halogen atom,

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and n' is 2 or 3,

with a compound or compounds, of formula (V)

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HOR

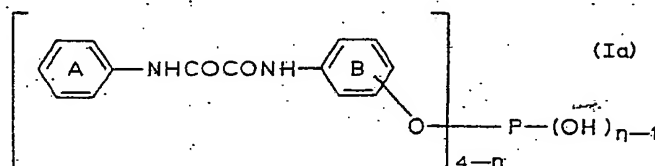
(V)

wherein R is as defined in Claim 1, in a molar ratio of 1: $n'-1$.

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9. A process according to Claim 8 for the production of an organic phosphorus compound of formula (Ia)

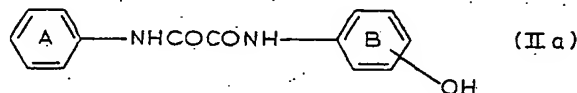
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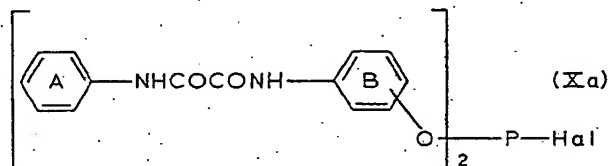
wherein n is 1 or 2,

each benzene nucleus A, independently, is unsubstituted or substituted by one or two alkyl radicals containing not more than 9 carbon atoms, by one or two alkoxy radicals containing not more than 16 carbon atoms and/or by one hydroxyl group which is in the ortho position with respect to the N atom or to a tertiary alkyl radical.

and each benzene nucleus B, independently, is unsubstituted or substituted by a methyl group, which comprises, when n is 1, condensing a compound or different compounds, of formula (IIa)



wherein the benzene nuclei A and B are as defined above, with phosphorus trichloride or phosphorus tribromide in the molar ratio 3:1, or, when n is 2, reacting a compound of formula (Xa)



wherein the benzene nuclei A and B are as defined above,

and Hal is a halogen atom, with water in equimolar proportions.

10. A process according to either of Claims 8 or 9, substantially as herein described with particular reference to any one of the Examples.

11. A method of improving the stability of an organic material against the action of ultraviolet light, visible light, heat or air, which comprises admixing with the organic material from 0.01 to 5% by weight of at least one compound of formula (I), as defined in Claim 1.

12. A method according to Claim 11, substantially as herein described with particular reference to any one of the Examples of Application a) to d).

13. An organic material which contains at least one compound of formula (I) or (Ia), as defined in Claims 1 and 9, respectively, as a stabilizer against the action of ultraviolet light, visible light, heat or air.

14. An organic material according to Claim 13, which contains as a stabilizer against the action of ultraviolet light, visible light, heat or air at least one compound of formula (I) or (Ia) along with at least one further stabilizer or costabilizer against the action of ultraviolet light, visible light, heat or air.

15. An organic material according to Claim 13, substantially as herein described with particular reference to any one of the Examples of Application a) to d).

MEWBURN ELLIS & CO.,

Chartered Patent Agents,

70-72, Chancery Lane,

London, W.C.2.

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